Reaction of Ketene with Ethylacetoacetate in the Presence of Some Organic Bases

AUTHOR(S):

Nodzu, Ryuzaburo; Isoshima, Toshizo

CITATION:

Nodzu, Ryuzaburo ...[et al]. Reaction of Ketene with Ethylacetoacetate in the Presence of Some Organic Bases. Bulletin of the Institute for Chemical Research, Kyoto University 1954, 32(1): 37-37

ISSUE DATE:

1954-01-31

URL:

http://hdl.handle.net/2433/75400

7. Reaction of Ketene with Ethylacetoacetate in the Presence of Some Organic Bases

Ryuzaburo NODZU and Toshizo ISOSHIMA

(Nodzu Laboratory)

In the previous paper (This Bulletin, **31**, 382(1953)), it was reported that ketene reacts with ethylacetoacetate to give C-acetyl derivative $CH_3COCHCOOC_2H_5$ (with $COCH_3$) or O-acetyl derivative $CH_3C(OCOCH_3)=CHCOOC_2H_5$ according to the reaction conditions.

Some organic bases, i. e. dimethylaniline, quinoline, pyridine, triethylamine and piperidine accelerated the reaction of ketene with ethylacetoacetate.

With these catalysts, O-acetylation occurred mainly when the reaction was carried out under cooling with ice, but C-acetylation predominated when they reacted under warming on a steam bath.

Pyridine alone, however, gave the product rich in O-acetyl derivative, even under warming.

It seemed that there is no relation between K_B of the bases and the reaction types.

The results of experiments are summarized in the table on page 36.

---

8. Reactions of Ketne with Compounds Containing Active Methylenic Hydrogen

Ryuzaburo NODZU and Toshizo ISOSHIMA

(Nodzu Laboratory)

It was already reported that the reaction of ketene with ethylacetoacetate or its sodium salt gave C-acetyl derivative in the absence of catalyst, and in the presence of sulfuric acid, O-acetyl derivative was sole product (This Bulletin **31**, 382 (1953)).

There is no information about the formation of C-acetyl derivatives in the reaction of ketene with *compounds containing active methylenic hydrogen* (henceforth abbreviated as compds. cont. A. M. H.).

Now, in our experiments, ketene and some compds. cont. A. M. H., i. e. acetylacetone, ethylmalonate, ethylcyanoacetate and malononitrile as well as ethylacetoacetate, gave C-acetyl derivatives or O-acetyl derivatives, according to the reaction conditions.